Low temperature photoluminescence characteristics of Zn-doped InP grown by metalorganic chemical vapor deposition

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Zn-doped InP layers were obtained by two different doping techniques: *in situ* doping by low pressure metalorganic chemical vapor deposition, and thermal diffusion from a Zn-containing film. Their low temperature photoluminescence (PL) characteristics were studied, and compared. In Zn-diffused InP, the deep donor to acceptor transition was the most dominant transition and other transitions such as the band edge transition and the band to band or shallow donor to acceptor transition were not observed at the excitation power of 10 mW. On the other hand, well resolved band edge peaks and the band or shallow donor to acceptor transition peak were observed for *in situ* Zn doped InP, implying that less interstitial Zn atoms were generated during *in situ* doping. Saturation of the hole concentration at 1.5×10^{18} cm^3 was observed in *in situ* Zn doped InP, and the changes in PL characteristics at the saturation level were extensively studied. Two new deep bands at 0.88–1.0 eV and 1.21–1.27 eV were observed, and the intensity of the lower energy band increased with diethylzinc flow rate. The lower energy band was observed even at room temperature, and it is presumed to be related with the saturation of hole concentration. © *1998 American Institute of Physics.* [S0021-8979(98)06204-5]

I. INTRODUCTION

Zn is one of the most important *p*-type dopants in InP and its related compound semiconductors widely used in optoelectronic device fabrication. Diffusion[1,2] and *in situ* doping[3,4] are normally used for Zn doping. It was reported that the hole concentration in Zn-diffused InP was 0.5%–10% of the total Zn concentration.[2] After high-temperature activation anneals, the hole concentration increased to the value comparable to the Zn concentration. Zn diffusion is known to go on through an interstitial-substitutional kick-out mechanism,[5,6] in which interstitial Zn atoms are generated.[1,2] A substitutional Zn atom in an In site behaves as a shallow acceptor, while a Zn atom in an interstitial site behaves as a deep donor. It is now widely accepted that the small hole concentration in a Zn-diffused sample is attributed to the self-compensation of Zn acceptors by interstitial deep donors.[1,2] In *in situ* Zn doping by metalorganic chemical vapor deposition (MOCVD), the doping efficiency was reported to be very low due to the high equilibrium vapor pressure of Zn. Moreover, the hole concentration saturated approximately at $1-2\times10^{18}$ cm^3 levels,[7] presumably due to a similar self-compensation mechanism.

Photoluminescence (PL) is a characterization technique used frequently for the study of the band structure and the carrier recombination mechanism in III–V semi conductors.[8,9] A characteristic donor-acceptor transition, resulting from the presence of interstitial Zn atoms, was reported for the Zn-doped InP.[1,2] PL characteristics for the *in situ* Zn-doped InP was also reported,[8] however, the PL characteristics for samples doped close to or at the doping saturation level have not been reported yet.

In this paper, the low-temperature PL characteristics of the *in situ* Zn-doped InP at various doping levels is reported. InP samples were grown by low pressure metalorganic chemical vapor deposition (LP-MOCVD) with diethylzinc (DEZn) as a dopant source. Their temperature-dependent PL characteristics were compared with those of Zn-diffused InP samples.

II. EXPERIMENT

InP samples were grown by LP-MOCVD in a horizontal quartz reactor. A graphite susceptor was heated by rf induction and the wafer temperature was calibrated by infrared interference measurement.[10] Trimethylindium (TMIn) and PH_3 (99.9997%) were used as an indium and a phosphorus source, respectively. Diethylzinc (DEZn) was used as a Zn dopant source. Palladium-purified H_2 was used as a carrier gas and its total flow rate was fixed at 12 slm. Semi-insulating (100) InP substrates (Fe-doped) were cleaned sequentially in trichloroethane, acetone, and methanol for 10 min, each with ultrasonic agitation and finally rinsed with deionized water. They were etched in 5 H_2SO_4: 1 H_2O_2 : 1 H_2O solution and rinsed with deionized water, and finally cleaned *in situ* for 5 min at 620 °C in a PH_3 ambient. 2 μm thick Zn doped InP layers were grown at reactor pressure of 76 Torr and growth temperature of 620 °C. Flow rates of TMIn and PH_3 were held constant at 0.91 sccm and 218 sccm, respectively, with a growth rate of 3.4 μm/h. DEZn flow rates were varied from 0.01 sccm to 0.36 sccm in this study.

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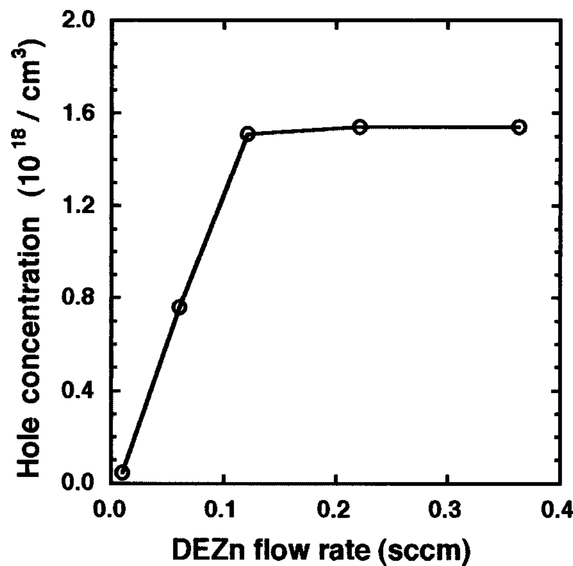

FIG. 1. Changes in hole concentration of *in situ* doped InP with DEZn flow rate. Growth conditions were: total pressure 76 Torr, substrate temperature 620 °C, TMIn flow rate 0.91 sccm, and PH_3 flow rate 182 sccm for all samples.

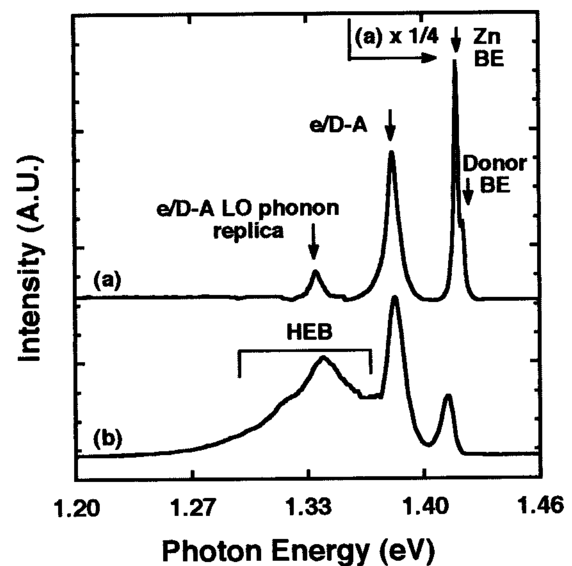

FIG. 2. 9 K PL spectra obtained from *in situ* Zn doped InP layers with hole concentrations below the saturation level of 1.5×10^{18} cm^3. The excitation power was fixed at 10 mW for all samples. Hole concentrations were (a) 4.6×10^{16} cm^3 at DEZn flow rate of 0.01 sccm, and (b) 7.6×10^{17} cm^3 at DEZn flow rate of 0.06 sccm.

For the Zn diffusion study, n-type (100) InP wafers (carrier concentration 1×10^{16} cm^3) were etched with a diluted HF solution before the thermal evaporation of 100 nm Zn_3P_2 film. A SiO_2 capping layer (100 nm) was deposited subsequently by plasma enhanced chemical vapor deposition to prevent outdiffusion of the diffusion source. Rapid thermal diffusion was performed in a quartz tube under N_2 ambient. The diffusion time was fixed at 15 min for all samples, while the diffusion temperature was varied from 450 to 650 °C. After the diffusion process, the residual dielectric film and the diffusion source were removed in dilute HF and a HNO_3 solution, respectively. Hole concentrations of Zn-doped InP layers were measured by an electrochemical $C-V$ profiler. Samples were excited by an Ar^+ ion laser, and the photoluminescence was dispersed in a double monochromater and detected by a Ge photodiode cooled by liquid nitrogen.

III. RESULTS AND DISCUSSION

InP epilayers were grown at 620 °C at various DEZn flow rates. The hole concentration in Zn-doped InP increased linearly with the DEZn flow rate as shown in Fig. 1, but reached a saturation hole concentration at approximately 1.5×10^{18} cm^3. Similar saturation behavior for *in situ* Zn doping was previously reported by other researchers,[7] but little was discussed about its physical origin. Hole concentrations greater than 3×10^{18} cm^3 in the Zn-diffused InP were reported, however, the actual Zn concentrations measured by secondary ion mass spectrometry were much higher than the hole concentration.[2,7] These results imply that a kind of compensation mechanism limits the maximum available hole concentration for the Zn-doped InP. Zn deep donors at interstitial sites are most responsible for the compensation, judging from low temperature PL experiments on Zn diffused and annealed InP layers.[1,2]

Figure 2 shows 9 K PL spectra measured for *in situ* Zn-doped InP layers with hole concentrations below the saturation limit of 1.5×10^{18} cm^3. The excitation power was 10 mW. Well-resolved band edge peaks are shown for the sample (a) with hole concentration of 4.6×10^{16} cm^3 at DEZn flow rate of 0.01 sccm. These peaks are a donor bound exciton peak at 1.417 eV and a strong Zn bound exciton peak at 1.414 eV. The intensity of the e/D-A peak (transition from the band or a shallow donor level to an acceptor level) at 1.378 eV, corresponding to an ionization energy of 42 meV (Ref. 9) for a Zn acceptor, was weaker than that of the Zn bound exciton peak due to the low doping concentration. The intensity of the e/D-A peak increased with doping concentration and exceeded that of the band edge peak at 1.408 eV when the hole concentration increased to 7.6×10^{17} cm^3 as in sample (b) grown at a DEZn flow rate of 0.06 sccm.

A weak peak at 1.334 eV was observed in sample (a), but its intensity increased abruptly as the hole concentration increased to 7.6×10^{17} cm^3, as in sample (b). Excitation power was varied to investigate the nature of the 1.334 eV peak. As the excitation power increased, the energy of the peak indexed as high-energy band (HEB) in sample (b) increased from 1.295 eV at 2 mW to 1.367 eV at 50 mW, as shown in Fig. 3. A peak shift of 50 meV/decade was observed. On the other hand, the e/D-A peak and the band edge peak at 1.408 eV showed no energy shift with excitation power. This large energy shift of the HEB with excitation power is a typical characteristic of a distant deep donor to an acceptor (D-A) transition.[11,12] Moreover, the peak position of the HEB matches the results reported for the Zn-diffused InP.[1,2] Thus, the broad HEB in sample (b) with hole concentration of 7.6×10^{17} cm^3 was assigned as a distant D-A peak. However, the 1.334 eV peak in sample (a) with hole concentration of 4.6×10^{16} cm^3 showed no energy shift with excitation power. The energy difference between this

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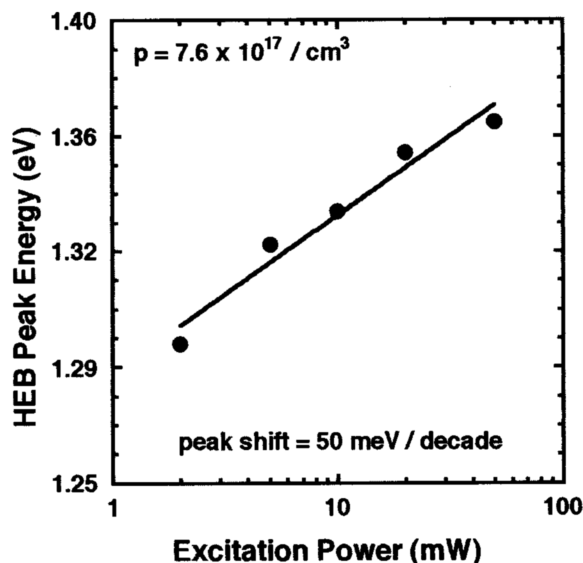

FIG. 3. Peak energy shift of the HEB band with excitation laser power for an InP epilayer with hole concentration of 7.6×10^{17} cm^3. Measurement temperature was 9 K.

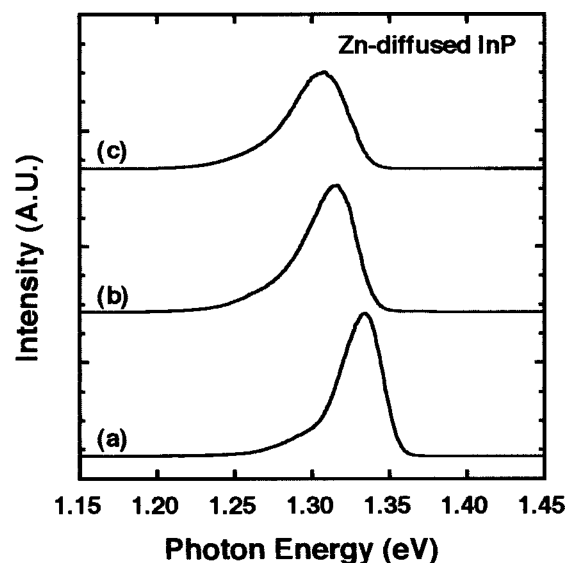

FIG. 4. PL spectra obtained from Zn-diffused InP samples at various hole concentrations. For Zn diffusion, Zn_3P_2 was used for a diffusion source and an undoped InP wafer was used for substrates. Excitation laser power was 10 mW and the sample temperature was 9 K for all samples. The hole concentration and diffusion temperatures were (a) 8.0×10^{16} cm^3 at 450 °C, (b) 7.5×10^{17} cm^3 at 550 °C, and (c) 3×10^{18} cm^3 at 650 °C, respectively.

peak and the e/D-A peak was 44 meV and this energy corresponds closely to the longitudinal optical (LO) phonon energy of InP, 42.8 meV.[13] Accordingly, the 1.334 eV peak in sample (a) was assigned as an LO phonon replica of the e/D-A peak.

At this point, it is interesting to compare the PL spectra for the Zn-doped InP at corresponding doping levels but doped by different doping techniques: *in situ* doping and diffusion. Remarkable differences in PL characteristics were observed between the two doping techniques. For the case of Zn diffusion the strongest peak in the PL spectra is a distant deep D-A transition peak observed in the range of 1.29 and 1.38 eV depending on doping levels, as shown in Fig. 4. The amount of blue shift of the peak energy with excitation power was around 19–25 meV/decade. Neither band edge nor e/D-A transition peaks were observed for all diffused samples at the excitation power of 10 mW. Weak e/D-A peaks were observed at higher excitation power, however, no band edge peaks were observed.

Assume that there are three carrier recombination paths in InP such as band edge transitions, e/D-A transitions, and distant deep D-A transitions. At low temperatures such as 9 K as in this PL study, electrons and holes tend to reside at more stable, lower energy states. Accordingly, transitions involving lower energy states become dominant and the intensities from the transitions become stronger. For the *in situ* doped InP (Fig. 2), the intensity of the deep D-A transition becomes stronger with doping concentration, however, peaks from the band edge and e/D-A transitions are still dominant, while no such transitions are visible from the Zn-diffused InP, shown in Fig. 4(b), at a comparable hole concentration. This implies clearly that the concentration of deep donors is higher in the Zn-diffused InP at comparable doping levels.

A few deep D-A transition peaks were reported in Zn doping of InP, and they are summarized in Table I. The origin of deep donors in Zn-diffused InP is generally known as interstitial Zn atoms, and the observed energy of the distant deep D-A transition peak ranges from 1.29 to 1.38 eV.[1,2] Similar transition peaks were also observed in our *in situ* doped samples as well as diffused samples. However, the magnitude of blue shift in Zn-diffused InP with excitation power in this study was about 19–25 meV/decade, about two times larger than 15 meV/ decade of Ref. 1 and 10 meV/ decade of Ref. 2. In the case of *in situ* doped InP, the amount of blue shift was as large as 50 meV/decade. It is not clear at the moment whether the differences in the magnitude of the blue shift are attributed to the difference in defect centers, or the differences in sample quality. More studies are needed to identify the origin of these differences.

Regardless of its origin, it seems clear that the concentration of deep donors is much lower in *in situ* doped InP and the difference is thought to be resulted from the difference in doping mechanisms. When InP layers are doped by diffusion, Zn diffusion goes in by an interstitial-substitutional kick-out mechanism[1,2,5,6] and consequently the concentration of interstitial Zn atoms is very high. In *in situ* doping, however, Zn atoms compete with In atoms for group III sublattice sites during the doping process. Furthermore, the incorporation efficiency of Zn is very low due to its high vapor pressure. Thus, Zn is most likely to be incorporated into the most stable substitutional sites than interstitial sites.

TABLE I. Distant donor-acceptor transitions in Zn-doped InP.

Transition	Emission energy (eV)	Reference
D-A (diffusion)	1.3–1.37	1
D-A (diffusion)	1.298–1.37	2
D-A (diffusion)	1.29–1.38	this exp.
HEB (*in situ*)	1.295–1.367	this exp.

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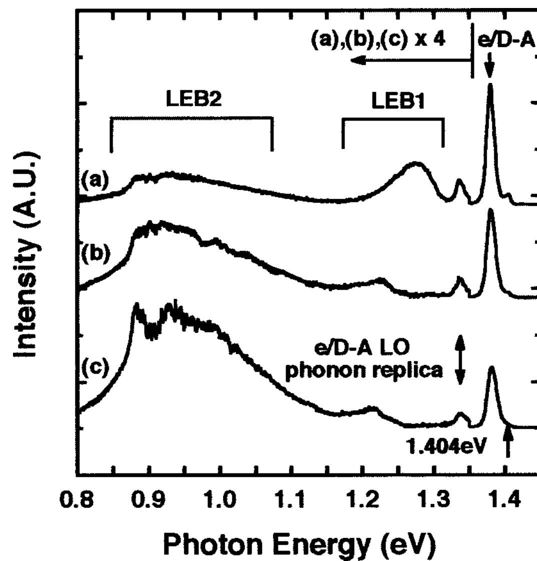

FIG. 5. PL spectra obtained from *in situ* Zn-doped InP epilayers at hole saturation concentration of 1.5×10^{18} cm^3. Excitation laser power was 10 mW and sample temperature was 9 K for all samples. DEZn flow rates were (a) 0.12 sccm, (b) 0.22 sccm, and (c) 0.36 sccm, respectively.

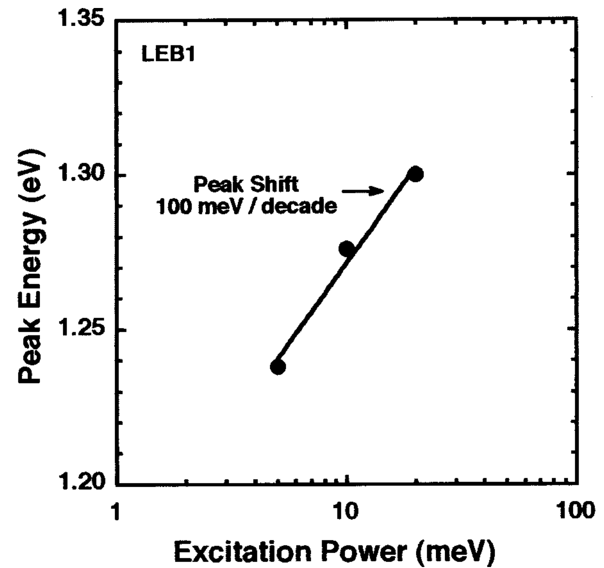

FIG. 6. Peak energy of the LEB1 band at various excitation laser powers. DEZn flow rate and the hole concentration were 0.12 sccm and 1.5×10^{18} cm^3, respectively.

However, even in *in situ* Zn-doped InP, the hole concentration becomes saturated at high doping levels. This implies that a kind of compensation mechanism plays an important role. To understand the compensation mechanism, PL measurements were made for the samples with a saturated hole concentration of 1.5×10^{18} cm^3, as shown in Fig. 5. Samples shown here had the same hole concentrations, but the actual DEZn flow rates during growth were varied. The flow rates were (a) 0.12 sccm, (b) 0.22 sccm, and (c) 0.36 sccm, respectively. Comparison of Fig. 5 with Fig. 2 revealed some different features in PL spectra between samples at the hole saturation level and samples below the hole saturation level. The intensity of the e/D-A transition peak at 1.380 eV, one of the most dominant transitions in *in situ* Zn-doped InP, decreased as the DEZn flow rate increased without affecting the hole concentration. The intensity of the band edge peak at 1.404 eV, observed for the sample grown at the DEZn flow rate of 0.12 sccm, decreased with DEZn flow rate. No distant deep D-A transition peaks were observed in the 1.29–1.35 eV range as in Zn-diffused samples. Instead, two other bands, indexed as low energy band No. 1 (LEB1) and low energy band No. 2 (LEB2) were observed. These two bands were never observed in *in situ* doped InP at DEZn flow rates lower than 0.12 sccm. The energy ranges of LEB1 and LEB2 were from 1.21 to 1.27 eV and 0.882 to 1 eV, respectively.

The peak of the LEB1 band shifted to lower energy as the DEZn flow rate increased, however, its intensity decreased. Such a decrease in intensity of LEB1 was attributed to the abrupt increase in intensity of LEB2 associated with deeper transition centers. The peak energy of the LEB1 was also shifted by 100 meV/decade with excitation power, as shown in Fig. 6. This result indicates that the LEB1 band results from a donor to acceptor transition, and the centers involved in this transition have deeper energy levels than those involved in the distant deep D-A transition (HEB) found below the hole saturation concentration. On the other hand, the intensity of the LEB2 band increased with DEZn flow rate, but the band showed no energy shift with excitation power.

These abrupt changes in PL spectra have never been reported for *in situ* Zn-doped InP, and it is presumed that there should be a change in the dominant recombination path near the hole saturation level of 1.5×10^{18} cm^3. Below the saturation level, Zn deep donors at interstitial sites and Zn acceptors are the most stable sites for electrons and holes, respectively, and they predominantly recombine via these recombination centers. At the saturation level, however, the PL spectra in Fig. 5 and Fig. 2 clearly show that the carrier

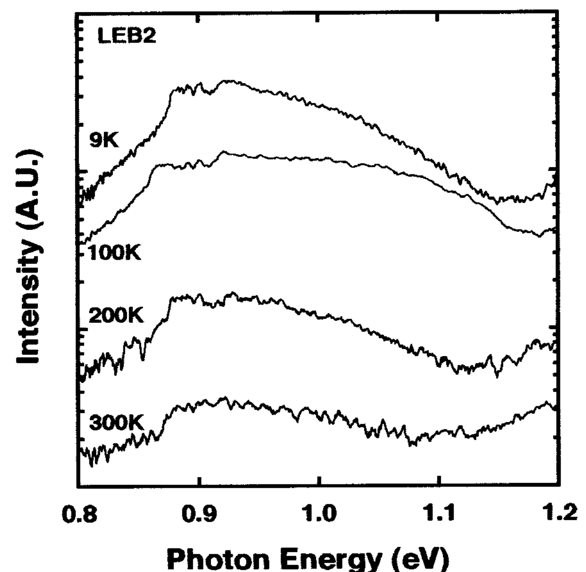

FIG. 7. Changes in LEB2 with temperature. The PL spectra were obtained from the *in situ* doped InP with hole concentration of 1.5×10^{18} cm^3 and DEZn flow rate of 0.12 sccm. PL measurement temperatures were (a) 9 K, (b) 100 K, (c) 200 K, and (d) 300 K.

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TABLE II. LEB2 and hole traps determined by other techniques. For LEB2 band, the binding energies were calculated from the two distinguishable peaks having emission energies of 0.85 and 0.93 eV.

Peak	Measuring technique	Binding energy (eV)	Reference
Hole trap	TSCAP	$E_v+0.59$	14
Hole trap	TSCAP	$E_v+0.62$	14
Hole trap	TSCAP	$E_v+0.59$	15
Hole trap	DLTS	$E_v+0.56$	16
LEB2	PL	$E_v+0.54$	this exp.
LEB2	PL	$E_v+0.49$	this exp.

recombination path changes from HEB and band edge to LEB1 and LEB2 bands. As the doping concentration approaches a saturation level, new deep centers related with LEB1 and LEB2 begin to form and the recombination occurs more efficiently through these deeper centers.

PL spectra of the InP sample grown at DEZn flow rate of 0.12 sccm were measured at various temperatures. The e/D-A peak overlapped with band edge peaks as the temperature increased, and eventually, only the band edge peak was found at temperatures higher than 200 K. The LEB1 peak also overlapped with HEB and finally disappeared at temperatures higher than 150 K. At room temperature the HEB peak disappeared. Nevertheless, LEB2 did not disappear even at room temperature, as shown in Fig. 7. The fact that the LEB2 band exists even at 300 K is very important because it implies that this band effectively captures carriers even at room temperature and remains as an effective recombination center. Energy levels close to the LEB2 were reported in Zn-doped InP by other techniques such as thermally stimulated capacitance (TSCAP) and deep level transient spectroscopy (DLTS). Various hole traps were reported,[14–16] and their energy levels are summarized in Table II.

At this time, the physical origins for LEB1 and LEB2 bands are not clear. In our experiments, excessive supply of Zn at high DEZn flow rates may foster local precipitation of Zn_3P_2 which is known to be energetically stable near 900 K.[17] Local strain energy from the precipitate in the zinc blende structure can be lowered by P vacancy formation, or P vacancies can be formed in the InP matrix due to the precipitate formation. Montie *et al.* observed two bands after annealing of the Zn-diffused InP samples[2]; one is a distant D-A band around 1.3 eV, the other is the peak observed in the similar energy range with the LEB1 band in this study. It was speculated that the band might be related with P vacancies formed during annealing. No report has been made for LEB2. It may also be related with the precipitation and P vacancy formation with high Zn content, however, more studies need to be done to identify the physical origin.

IV. CONCLUSION

In situ Zn-doped InP samples were grown by LP-MOCVD at 620 °C at various doping levels. The hole concentration of *in situ* doped InP showed saturation behavior at 1.5×10^{18} cm^3. The samples were investigated by low temperature PL measurements and the PL spectra were compared with those of Zn-diffused InP samples. In Zn-diffused InP samples, distant deep D-A peaks were observed and the intensity of the e/D-A transition peak was much smaller than that of the distant deep D-A peak. No band edge peaks were observed. In contrast, *in situ* Zn-doped samples had well-resolved band edge peaks, e/D-A peak, and distant deep D-A peak, among which the e/D-A peak was strongest. These results can be explained by the lesser generation of interstitial Zn atoms during *in situ* doping.

For *in situ* doped samples at the hole saturation level, a distant deep D-A transition peak disappeared and the new two bands, LEB1 (1.21 eV–1.27 eV) and LEB2 (0.88 eV–1.0 eV) emerged instead. From the investigation on the characteristics of LEB1 and LEB2 bands at various temperatures, excitation powers and DEZn flow rates, it was found that these two bands were related with the saturation of hole concentration.

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